



# A novel anthracene-appended triazolium for fluorescent sensing to $\text{H}_2\text{PO}_4^-$



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## ABSTRACT

A novel anthracene-based anion receptor **1** bearing two 1,2,3-triazolium donor groups has been designed and synthesized. In competitive solvents, compound **1** shows effective selectivity toward  $\text{H}_2\text{PO}_4^-$  in a fluorescence enhancement effect, with no interference from other anions.

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Phosphate ions and their derivatives play essential roles in signal transduction and energy storage in biological systems.<sup>1</sup> On the other hand when present in excess in waterways, they can be highly toxic via eutrophication.<sup>2</sup> Therefore, the selective recognition and sensing of phosphates are of great importance to researchers. During the past decades, many synthetic receptors incorporating neutral NH hydrogen bond donor groups (e.g., pyrrole, indole, urea, thiourea, and amide), as well as the cationic charge-based anion receptors (e.g., ammonium, guanidinium, and imidazolium), have been well established.<sup>3</sup> However, to the best of our knowledge, triazolium-based anion receptors, especially fluorescent triazolium derivatives with the  $(\text{C}-\text{H})^+\cdots$ anion hydrogen bond donors, have not yet to be exploited for the purpose of phosphate anion recognition.

'Click reaction' produced 1,2,3-triazoles and their alkylation derivatives (triazoliums) have been exploited in the synthesis of a vast array of materials for its high efficiency, mild reaction conditions, and technical simplicity.<sup>4</sup> Recently studies have demonstrated that some acyclic and macrocyclic bis- and poly-triazoles can bind anions in organic solvents through triazole  $\text{C}-\text{H}\cdots$ anion interactions,<sup>5</sup> and were found to have a high affinity and selectiveness for chloride ion over other anions.<sup>6</sup> Furthermore, the anion binding capacity can be enhanced by converting a triazole unit into

a triazolium cation possessing strong  $(\text{C}-\text{H})^+\cdots$ anion charged hydrogen bonding interaction.<sup>7</sup>

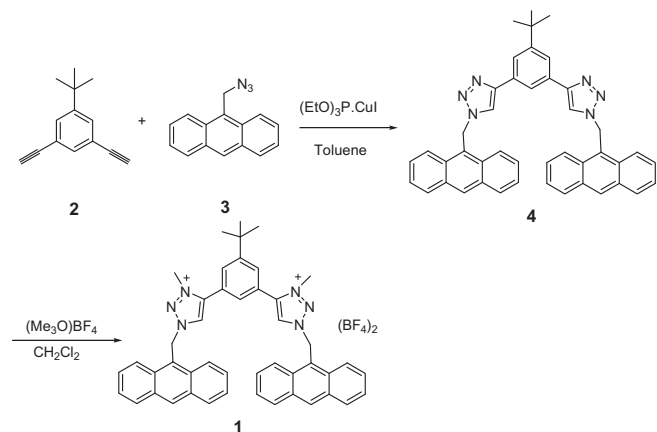
Pandey and co-workers have reported some cyclic and acyclic bile acid-based 1,2,3-triazolium receptors, which showed high affinity and selectivity toward phosphate anion over other anions.<sup>8</sup> However, the absent easily detectable optical and/or electrochemical units, which undergo readily discernible changes in these signals after binding with a given guest species, limited these systems in practical applications. These design criteria make systems based on anthracene attractive. Anthracene is one of the most useful fluorogenic units because of its characteristic and sensitive emissions from both the monomer and the excimer emission. Anthracene-based receptors for anion recognition have been reported widely.<sup>9,10</sup>

Taking advantage of the strong  $(\text{C}-\text{H})^+\cdots$ anion interaction between the triazolium and anions and good fluorescent properties of anthracene, we thus envisioned that plugging the anthracene unit into the triazolium could provide novel fluorescent chemosensors for anions. With this purpose in our mind, a novel anthracene-containing 1,2,3-triazolium receptor **1** (Scheme 1) has been designed and synthesized. To the best of our knowledge, compound **1** is the first example of fluorescent triazolium-base receptor, which shows effective selectivity for  $\text{H}_2\text{PO}_4^-$  over other anions. Upon the addition of  $\text{H}_2\text{PO}_4^-$  in competitive polar organic  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{OH}$  (9:1, V/V) solvent, compound **1** shows a large enhancement of its fluorescence.

The synthetic route of **1** is shown in Scheme 1. Firstly, we synthesized the key precursors 5-*tert*-butyl-1,3-diethynylbenzene **2**<sup>5c</sup> and 9-anthracenylmethyl azide **3**<sup>11</sup> by the literature methods. Then using 'click reaction',<sup>12</sup> **4** was easily prepared in high yield

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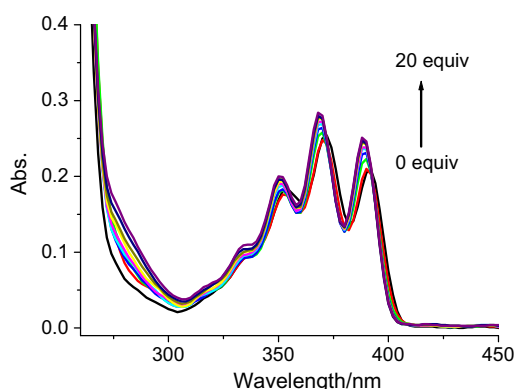


**Scheme 1.** Preparation route of **1**.

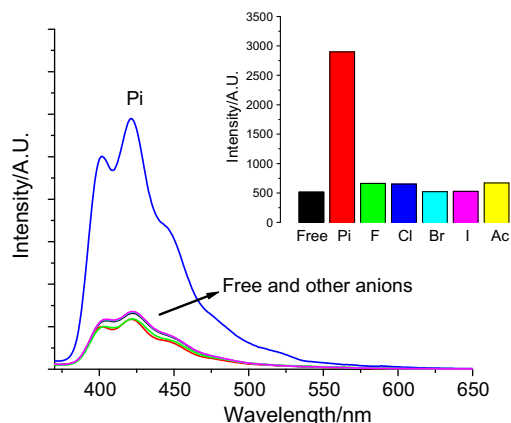
(86%) by a coupling reaction of **2** and **3** in toluene under reflux with  $(\text{EtO})_3\text{P}_3\cdot\text{CuI}$  as a catalyst. The triazolium receptor **1** was then obtained by alkylation of **4** with trimethyloxonium tetrafluoroborate in dichloromethane solution. Its molecular structure was confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, HR-MS, and elemental analysis.

The recognition ability of **1** toward various anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{H}_2\text{PO}_4^-$ ) in the form of their corresponding tetrabutylammonium salts ( $\text{TBA}^+$ ) was first investigated by the UV–vis spectroscopy in competitive organic solution ( $\text{CH}_2\text{Cl}_2$ – $\text{MeOH}$ , 9:1). The absorption spectra of **1** were hardly affected by  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{CH}_3\text{COO}^-$ , which indicated weak binding ability between **1** and these anions. On the other hand, addition of  $\text{H}_2\text{PO}_4^-$  induced an apparent blue shift of the anthracene-base absorption bands of **1** (Fig. 1). This result implied not only the presence of strong interactions between **1** and  $\text{H}_2\text{PO}_4^-$  but also the formation of some interaction and association between anthracenes at the ground states.<sup>13</sup> Obviously three isosbestic points at 354, 372, and 391 nm indicated that only one species was formed during the complexation, which can also be proved by the emission titration result—only the monomer emission was observed during the addition of  $\text{H}_2\text{PO}_4^-$  to **1** (see below). Since the UV–vis spectra of **1** show relative a little change upon the addition of various anions, therefore its binding properties were investigated by the fluorescent spectroscopy.

The fluorescence spectra of **1** in the presence and absence of the aforementioned anions are shown in Figure 2. The free receptor **1** exhibits weak monomeric anthracene-based emission bands at 400, 421, and 443 nm. The relative weakly fluorescence intensity



**Figure 1.** UV–vis titration spectra of **1** ( $2 \times 10^{-5}$  M) upon addition of  $\text{H}_2\text{PO}_4^-$  in  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{OH}$  solution (9:1, V/V).



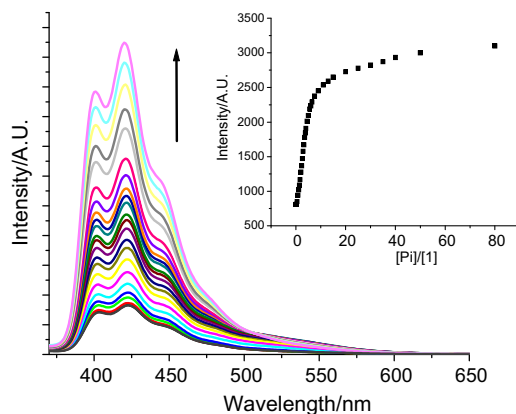
**Figure 2.** Emission changes of **1** ( $2 \times 10^{-5}$  M) upon addition of 50 equiv of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{H}_2\text{PO}_4^-$  (Pi) in  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{OH}$  (9:1, V/V) solution with excitation at 360 nm. Inset: fluorescence intensity in 421 nm of **1** in the presence of various anions.

of **1** may be ascribed to the quenching effect of a photo-induced electron transfer (PET) process from the anthracene moieties to the charged triazoliums. Same mechanism was also reported in some anthracene-appended pyridinium-based receptors for anions.<sup>14</sup> When an equal amount (50 equiv) of anions were added, only  $\text{H}_2\text{PO}_4^-$  induced a marked enhancement of **1**'s emission. In contrast, other anions showed little or almost no change of its emission, which is consistent with the UV–vis titration results. This result demonstrated that **1** exhibits high selectivity toward  $\text{H}_2\text{PO}_4^-$  in such competitive polar organic solvent by changing its fluorescent properties.

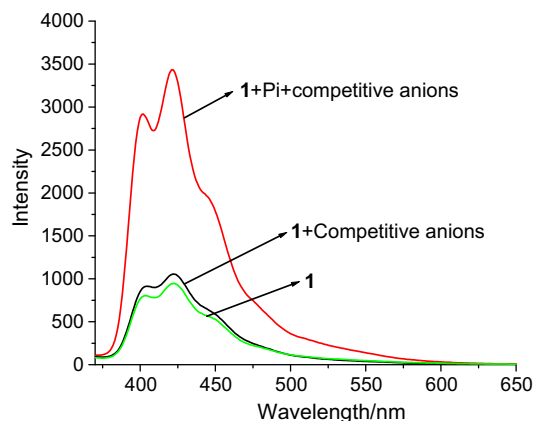
The binding constant between **1** and  $\text{H}_2\text{PO}_4^-$  was also determined by the fluorescent titration (Fig. 3). The 1:1 stoichiometry binding of **1** and  $\text{H}_2\text{PO}_4^-$  was confirmed by the fluorescence Job's plot. From the fluorescent titration data, the binding constant of **1** and  $\text{H}_2\text{PO}_4^-$  was calculated to be  $2.78 \times 10^3 \text{ M}^{-1}$  in the  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{OH}$  (9:1, V/V) solution.<sup>15</sup>

Besides the high sensitivity, another important feature of **1** is its high selectivity toward  $\text{H}_2\text{PO}_4^-$  over other competitive species. The competition experiment of **1** between  $\text{H}_2\text{PO}_4^-$  and other anions is shown in Figure 4. The presence of other anions does not cause any significant changes in the emission of **1** with  $\text{H}_2\text{PO}_4^-$ . This indicates that the selectivity of **1** for  $\text{H}_2\text{PO}_4^-$  over other competitive anions in the  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{OH}$  solution is remarkably high.

To seek detailed information on the binding mechanism of chemosensor **1** with  $\text{H}_2\text{PO}_4^-$ ,  $^1\text{H}$  NMR titration was carried out in  $\text{DMSO}-d_6$  solution (Fig. 5). Upon addition of  $\text{H}_2\text{PO}_4^-$  anion, a



**Figure 3.** Fluorescence titration spectra of **1** ( $2 \times 10^{-5}$  M) upon addition of  $\text{H}_2\text{PO}_4^-$  in  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{OH}$  solution (9:1, V/V) with excitation at 360 nm. Inset: fluorescence intensity of **1** ( $2 \times 10^{-5}$  M) at 421 nm versus  $\text{H}_2\text{PO}_4^-$  concentrations.

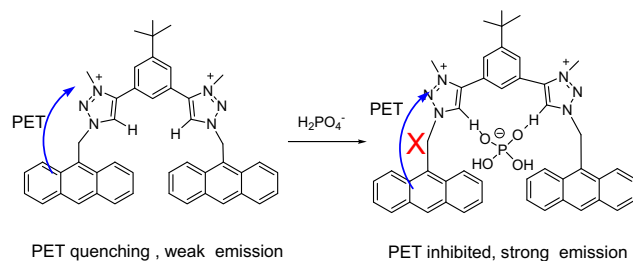


**Figure 4.** Fluorescence spectra of **1** ( $2 \times 10^{-5}$  M) with  $\text{H}_2\text{PO}_4^-$  (50 equiv) upon addition of various anions (100 equiv) in  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{OH}$  solution (9:1, V/V) with excitation at 360 nm.

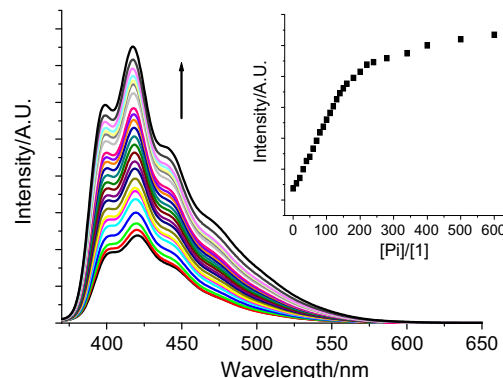
significant downfield shift in the triazolium (Ha) protons was observed in **1** (from 9.29 to 10.15 ppm, 0.9 ppm shifted when 2 equiv  $\text{H}_2\text{PO}_4^-$  was added), suggesting the complexation of the anion with  $(\text{C}-\text{H})^+ \cdots \text{anion}$  interaction. In addition, upon interaction, the methylene protons Hg ( $\Delta\delta = 0.16$  ppm) and anthracenyl protons Hc ( $\Delta\delta = 0.15$  ppm) show a little downfield shift, while other anthracenyl protons Hb ( $\Delta\delta = -0.23$  ppm), Hd ( $\Delta\delta = -0.18$  ppm), and Hf ( $\Delta\delta = -0.15$  ppm) show a little upfield shift, which may be attributed to the restricting bond rotation and/or  $\pi$ -stacking interaction between the pendant anthracenes in **1** for coordination.<sup>16</sup>

Based on above results, a proposed binding process of receptor **1** toward  $\text{H}_2\text{PO}_4^-$  is shown in Scheme 2. Before complexation with  $\text{H}_2\text{PO}_4^-$ , a strong PET process from the electron-rich anthracene moieties to the electron-deficient triazolium ions happens, and then quenches the anthracene-based fluorescence in **1**. While after binding  $\text{H}_2\text{PO}_4^-$ , the formation of the  $(\text{C}-\text{H})^+ \cdots \text{O}$  interaction would diminish acceptor properties of the triazolium ions, hence inhibit the PET process and recover the anthracene emission.

Previously, Yoon and Kim have reported various anthracene-based imidazoliums for fluorescent recognition anions via the  $(\text{C}-\text{H})^+ \cdots \text{anion}$  hydrogen bonds between the imidazolium moieties and anions.<sup>10</sup> It was found that these receptors exhibited selectivity toward  $\text{H}_2\text{PO}_4^-$  and  $\text{HP}_2\text{O}_7^{3-}$  over other anions. However, in most instances, binding phenomena of these receptors were observed via fluorescence quenching effect. As compared to these receptors, the present bistriazolium receptor seems to be more promising for



**Scheme 2.** A possible binding mechanism between **1** and  $\text{H}_2\text{PO}_4^-$ .



**Figure 6.** Fluorescence titration spectra of **1** ( $2 \times 10^{-5}$  M) upon addition of  $\text{H}_2\text{PO}_4^-$  in  $\text{DMSO}$ – $\text{H}_2\text{O}$  solution (95:5, V/V) with excitation at 360 nm. Inset: fluorescence intensity of **1** ( $2 \times 10^{-5}$  M) at 421 nm versus  $\text{H}_2\text{PO}_4^-$  concentrations.

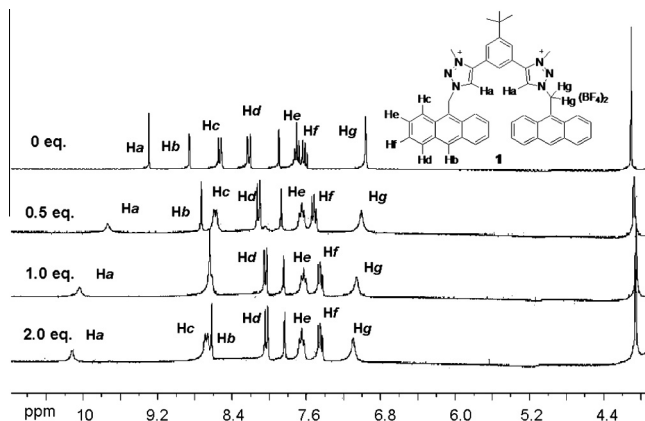
its fluorescence enhancement effect toward  $\text{H}_2\text{PO}_4^-$  over other anions. Fluorescence turn-on probes are considered to have more sensitivity than turn-off probes due to the lack of background signal.

To validate the selectivity of chemosensor **1** in aqueous solution, the fluorescence spectral changes of **1** upon the addition of various anions in  $\text{DMSO}$ – $\text{H}_2\text{O}$  (95:5, V/V) were measured (Fig. 6). The changes observed in the emission spectra of **1** were similar to those observed above in  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{OH}$  solution, where a dramatic fluorescence enhance upon interaction with  $\text{H}_2\text{PO}_4^-$ . However, the number of equivalents required to reach a plateau is high (more than 600 equiv), which indicates that in the highly competitive water solution, the complexation equilibrium toward the formation of the anionic complex is more difficult. Although **1** could not be used to detect  $\text{H}_2\text{PO}_4^-$  in 100%  $\text{H}_2\text{O}$ , the possibility of using **1** in  $\text{DMSO}$ – $\text{H}_2\text{O}$  (95:5, V/V) implies that **1** is strong enough to detect  $\text{H}_2\text{PO}_4^-$  in more polar environments.

In conclusion, a novel anthracene-based anion receptor **1** bearing two triazolium groups has been synthesized and characterized. We found that **1** shows high sensitive toward  $\text{H}_2\text{PO}_4^-$  over other anions in competitive solvents. Upon the addition of  $\text{H}_2\text{PO}_4^-$ , compound **1** displays a large enhancement of its fluorescence, which is attributed to strong  $(\text{C}-\text{H})^+ \cdots \text{anion}$  hydrogen bond between the two triazolium moieties and  $\text{H}_2\text{PO}_4^-$ . To our opinion, **1** is the first example of fluorescent triazolium receptor for anions in the literature. Designing based on the present studies can be further modified to construct more developed systems.

#### Acknowledgment

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**Figure 5.** Partial  $^1\text{H}$  NMR spectrum of **1** upon addition of various amounts of  $\text{H}_2\text{PO}_4^-$  in  $\text{DMSO}-d_6$  solution.

## Supplementary data

Supplementary data associated (experimental procedures and characterization data of compounds) with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2013.05.033>.

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